Fluorous biphasic catalysis. 2. Synthesis of fluoroponytailed amine ligands along with fluoroponytailed carboxylate synthons, $[M(C_8F_{17}(CH_2)_2CO_2)_2]$ (M = Mn^{2+} or Co^{2+}): Demonstration of a perfluoroheptane soluble precatalyst for alkane and alkene functionalization in the presence of *tert*-butyl hydroperoxide and oxygen gas

Jean-Marc Vincent, Alain Rabion, Vittal K. Yachandra, and Richard H. Fish

Abstract: Fluorous biphasic catalysis (FBC) is a relatively new concept for homogeneous catalysis where the fluorocarbon soluble catalyst resides in a separate phase from the substrate and products. Therefore, separation of the catalyst and the products occurs by a facile decantation process. In this contribution, we present the synthesis of new R_f-fluoroponytailed synthons, 2-iodo-1-perfluorooctyl-3-propanol (**1**), 3-perfluorooctyl-1-propanol (**2**), and 3-perfluorooctyl-1-iodopropane (**3**), a variety of new R_f-fluoroponytailed ligands (**4**–**8**), with starting amines, 1,4,7-triazacyclononane, bis-picolylamine, and bis-picolylaminoethylenediamine, as well as new R_fMn^{2+} and R_fCo^{2+} fluoroponytailed carboxylate synthons, $[Mn(O_2C(CH_2)_2C_8F_{17})_2]$ (**9**), and $[Co(O_2C(CH_2)_2C_8F_{17})_2]$ (**10**), where R_f is C_8F_{17}. The only totally perfluoralkane soluble ligand we found was 1,4,7-tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN, **4**), and it was utilized, along with synthons **9** and **10**, to generate in situ R_fMn^{2+}–R_fTACN and R_fCo^{2+}–R_fTACN complexes as precatalysts for functionalization of alkanes and alkenes. We will demonstrate that indeed this novel FBC approach for the separation of the precatalyst from the substrates and (or) products is viable for oxidation of alkanes and alkenes in the presence of the necessary oxidants, *tert*-butyl hydroperoxide (TBHP), and O_2 gas. We will also show that these oxidation reactions occur via an autoxidation mechanism under our FBC conditions, while using electron spin resonance (ESR) techniques to ascertain the redox chemistry occurring with the starting mononuclear R_fMn^{2+}–R_fTACN complex.

Key words: fluorous solvents, biphasic catalysis, alkane/alkene oxidation.

Résumé : La catalyse biphasique en milieu fluoré est un concept récent de catalyse homogène nécessitant l'emploi de catalyseurs solubles dans les perfluorocarbures. Le catalyseur se trouvant dans une phase différente du substrat et des produits de réaction, il peut être recyclé par une simple décantation. Nous présentons la synthèse de nouveaux synthons (**1**–**3**), et ligands (**4**–**8**), à chaîne perfluorée, ainsi que de nouveaux complexes métalliques à ligands carboxylates fluorés, $[Mn(O_2C(CH_2)_2C_8F_{17})_2]$ (**9**) et $[Co(O_2C(CH_2)_2C_8F_{17})_2]$ (**10**). Le ligand 1,4,7-tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN, **4**) est le seul ligand à être soluble dans les perfluorocarbures. A partir des composé **9** et **10** et du ligand **4**, les complexes R_fMn^{2+}–TACN et Co^{2+}–TACN générés in situ servent de précatalyseurs pour les oxydations d'alcanes et alcènes. Les réactions sont réalisées en milieu biphasique en présence des oxydants TBHP et O_2 et les produits sont facilement séparés du catalyseur par simple décantation. Dans les

Received September 1, 2000. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on July 5, 2001.

The senior author, RHF, wishes to dedicate this fluorous biphasic catalysis contribution to Brian James, a long-time friend and colleague, whose homogeneous catalysis studies/textbook have been an inspiration to several generations of chemists interested in this fascinating discipline.

J.-M. Vincent,[1] A. Rabion,[2] V.K. Yachandra, and R.H. Fish.[3] Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, U.S.A.

[1]Present address: Laboratoire de Chimie Organique et Organométallique, UMR CNRS 5802, Université Bordeaux 1, 351 Cours de la Libération, 33405 Talence CEDEX, France.
[2]Present address: Groupement de recherche de Lacq, BP 34, 64170 Artix, France.
[3]Corresponding author (fax: (510) 486-7303; e-mail: rhfish@lbl.gov).

 DOI: 10.1139/cjc-79-5/6-888

conditions utilisées les réactions se déroulent suivant un mécanisme radicalaire d'autoxydation.

Mots clés : solvants fluorés, catalyse biphasique, oxydation alcane/alcène.

[Traduit par la Rédaction]

Introduction

Recently, Horváth and Rábai (1) published an important paper on a new homogeneous catalysis concept, *fluorous biphasic catalysis* (FBC), that entailed the use of a fluorocarbon as one phase containing a modified fluoroponytailed catalyst, while the substrate and the product were soluble in a second hydrocarbon phase; this FBC concept was also reported in a Ph.D thesis that was not readily accessible by the catalysis community (2). More importantly, the Horváth and Rábai paper has been a virtual catalyst for chemists interested in new biphasic concepts, while this novel FBC approach has led to many contributions in a very short time frame (3). The process of developing a new paradigm for the separation of the homogeneous catalyst from the substrate and the product must start with the solvent system. Therefore, it is well-known that perfluorohydrocarbons have unusual properties that entail being extremely hydrophobic and lacking hydrogen bonding capabilities, which renders them to be relatively insoluble in their hydrocarbon analogs, and they are also able to dissolve various gases such as oxygen, hydrogen, and carbon dioxide, as examples (4). Thus, it is surprising that it took so long for this FBC approach to be discovered, since the above mentioned parameters would allow a number of critical catalytic reactions to be demonstrated using perfluorohydrocarbons as one phase in a biphasic solvent mode (1–3).

We have been interested in homogeneous oxidation catalysis for many years with the focus on functionalizing alkanes and alkenes at ambient temperatures (5). Our fascination with the FBC process provided an opportunity to also demonstrate this novel concept for the functionalization of alkanes and alkenes, and in a preliminary account (6), we did indeed verify this new biphasic approach for alkane and alkene functionalization, and in fact, a similar approach was also published by Pozzi et al. (7) very soon after. Therefore, in this full account, we present the synthesis of R_f-fluoroponytailed synthons (**1**–**3**), a variety of new R_f-fluoroponytailed ligands (**4**–**8**), with starting amines, 1,4,7-triazacyclononane (TACN), bis-picolylamine (BPA), and bis-picolylaminoethylenediamine (BisPICEN), as well as new R_fMn^{2+} and R_fCo^{2+} fluoroponytailed carboxylate synthons, $[Mn(O_2C(CH_2)_2C_8F_{17})_2]$ (**9**), and $[Co(O_2C(CH_2)_2C_8F_{17})_2]$ (**10**), where R_f is C_8F_{17}, and clearly demonstrate the critical need to pay close attention to the structures of the ponytailed ligands as it pertains to their solubility in perfluorocarbons.

To reiterate, we will further demonstrate the utilization of the FBC paradigm with the functionalization of alkanes and (or) alkenes, using in situ generated R_fMn^{2+}–R_fTACN and R_fCo^{2+}–R_fTACN as precatalysts that are totally soluble in the fluorous phase, and in the presence of the necessary oxidants, *tert*-butyl hydroperoxide (TBHP) and O_2 gas (6). In comparison to the new FBC concept presented in this paper, it is important to note that the oxidation of alkanes with TBHP in acetonitrile, and epoxidation of alkenes with hydrogen peroxide (H_2O_2) in acetone, were previously achieved in one homogeneous phase by the in situ preparation of Mn^{2+} catalysts, using 2,2′-bipyridine and tris-*N*-methyl-TACN ligands, respectively, and further state that separation of the Mn^{2+} catalyst from the product will be relatively difficult or impossible (8).

Results and discussion

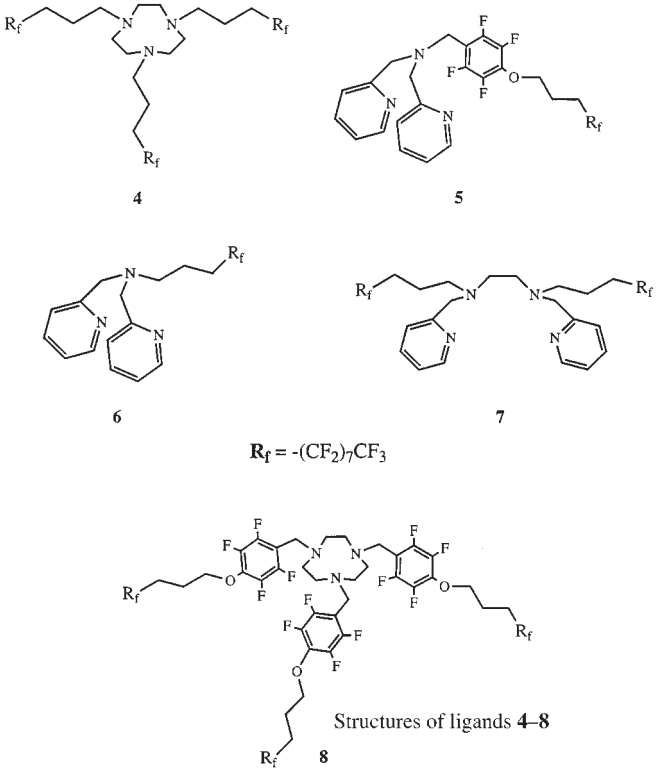
Synthesis of fluoroponytailed ligands 4–8

One of the key components of the FBC approach includes the synthesis of fluoroponytailed ligands that are totally soluble in fluorocarbon solvents at ambient temperature. Therefore, we set out initially to create a fluoroponytail synthon that we could append to our target ligands, which were aliphatic and aromatic substituted aliphatic amines. We chose aliphatic amines as ligands for several reasons that included their ease in appending fluoropontytails via alkylation reactions, and their metal complexes have been widely used in previous homogeneous oxidation chemistry of hydrocarbons (8). In our initial experiments to find a suitable fluoroponytailed synthon, we evaluated a compound that had a two-carbon spacer ($C_8F_{17}CH_2CH_2I$) but quickly found that in the presence of the aliphatic amine ligand that loss of HI prevailed rather than alkylation. Therefore, it is important to recognize that the three-methylene-carbon spacer in compound **3** was necessary, not only to insulate the amine from the powerful e-withdrawing effect of the perfluoroalkyl group, but also to avoid the above mentioned facile elimination reaction of HI that predominately occurs when a two-carbon spacer was used during the formation of ligands **4**–**8**.

The first step to the three-carbon spacer synthon, perfluoroalkyl iodide (**3**) proceeded by a free radical addition of a perfluoroalkyl iodide ($C_8F_{17}I$) to allyl alcohol that was initiated with AIBN to provide the perfluoroalkylated iodohydrin **1** (this procedure was slightly different than the one described by Kotora et al., who synthesized 3-perfluorohexyl-1-propanol ($C_6F_{13}(CH_2)_3OH$) using copper powder as a free radical initiator in neat solution followed by tin hydride reduction. See ref. 9). Compound **1** was then reduced to the perfluoroalkyl alcohol **2**, by using tributyltin hydride in dry benzotrifluoride. Iodination of **2** to form **3** was achieved using 85% phosphoric acid in the presence of phosphorous pentoxide and potassium iodide in 85% yield (Scheme 1).

The first alkylation approach we utilized to introduce the fluoroponytail, **2**, was the aromatic nucleophilic substitution with the *N*-pentafluorophenyl derivatives of the TACN and BPA ligands, leading to ligands **5** and **8** (Scheme 1). We introduced **2**, via a nucleophilic substitution of the *p*-fluoro substituent of the *N*-pentafluorophenyl group by using phase transfer catalysis in a mixture of 50% NaOH–trifluorotoluene, and in the presence of the phase transfer agent, Aliquat 336. The other alkylation approach, which directly alkylates

amine ligands (TACN), (BPA), and (BisPICEN) to provide **4**, **6**, and **7** with **3**, was conducted using K_2CO_3 in DMSO.



We were totally amazed to find that **4**, tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN), *was the only fluoroponytailed ligand found to be soluble in perfluorocarbons, such as perfluoroheptane (PFH) or perfluoromethylcyclohexane (PFMC), at room temperature.* Fluoroponytailed ligands **5**–**8**, with a fluorine content for **5**–**8** of <60% were only soluble in hot perfluorocarbons (~50°C), while **4** had a fluorine content of 64.2%. These results vividly demonstrate that polar groups such as a pentafluorophenyl group or a nonfluorinated pyridine have to be avoided to obtain good solublity in perfluorocarbons; these are extremely nonpolar solvents. It also shows that the solubilzation of ligands, and moreover, the subsequent metal complexes, could represent an important limiting step in the FBC approach for oxidation chemistry. Moreover, it is of interest to also note that **4** represented at that time, to our knowledge, the first example of an R_f–amine ligand (6) to be found to be soluble in a perfluorocarbon solvent, subsequently also verified by Pozzi et al. (7) with their tetra-azamacrocycle systems.

Synthesis of Mn^{2+} and Co^{2+} fluoroponytailed carboxylate complexes 9 and 10

To insure fluorcarbon solvent solubility of the metal complexes of ligand **4**, the only amine ligand we found to have total fluorocarbon solubility at ambient temperature, we thought that appending fluoroponytailed groups to the metal complexes we were going to utilize as synthons would help in this important aspect, since metal complexes with multiple charges and counter anions, such as ClO_4^-, NO_3^-, PF_6^-, would be very difficult to solubilze in perfluorocarbons. Therefore, the new R_fMn^{2+} and R_fCo^{2+} complexes $[Mn(C_8F_{17}(CH_2)_2CO_2)_2]$ (**9**) and $[Co(C_8F_{17}(CH_2)_2CO_2)_2]$ (**10**) were synthesized by reaction of $Mn(ClO_4)_2\cdot 6H_2O$ or $Co(ClO_4)_2\cdot 6H_2O$ in acetone with 2 equiv of the triethylammonium salt of the 3-R_f-alkylpropionic acid $C_8F_{17}(CH_2)_2CO_2H$; elemental analysis of **9** and **10** provided a metal:carboxylate ligand ratio of 1:2, while **9** was found to be slightly soluble in perfluorocarbons, exhibited an intense and broad ESR signal at $g = 2$ (9 K), and displayed the broad six-line hyperfine structure ($J = 90$ G). This could be attributed either to an oligomeric Mn^{2+} structure, consistent with a $Mn(OAc)_2$ trimeric structure, or a mononuclear Mn^{2+} complex of low solubility in perfluorocarbons at 9K (10). In addition, it appears that the carboxylate group is chelating, rather than being in a monodentate coordination mode, in agreement with the small difference ($\Delta\nu = 132$ cm^{-1}) observed in the IR spectrum of **9** between the asymmetric and symmetric C—O stretch ($\nu = 1578$ and 1446 cm^{-1}), respectively. Complex **10** had a similar IR spectrum as **9** and we suggest that the Co^{2+} analog has a similar structure as the Mn^{2+} complex.

Interestingly, when 1 equiv of **4** was added to a solution of **9** in perfluoroheptane, the complete solubilization of **9** occurred concomitantly with the appearance of a new UV absorption band at 320 nm tentatively suggesting that a new $[R_fMn(R_fTACN)]^{2+}$ complex (**11**) was formed in situ. A similar result was also achieved when ligand **4** and complex **10** were added together to provide $[R_fCo(R_fTACN)]^{2+}$ (complex **12**).

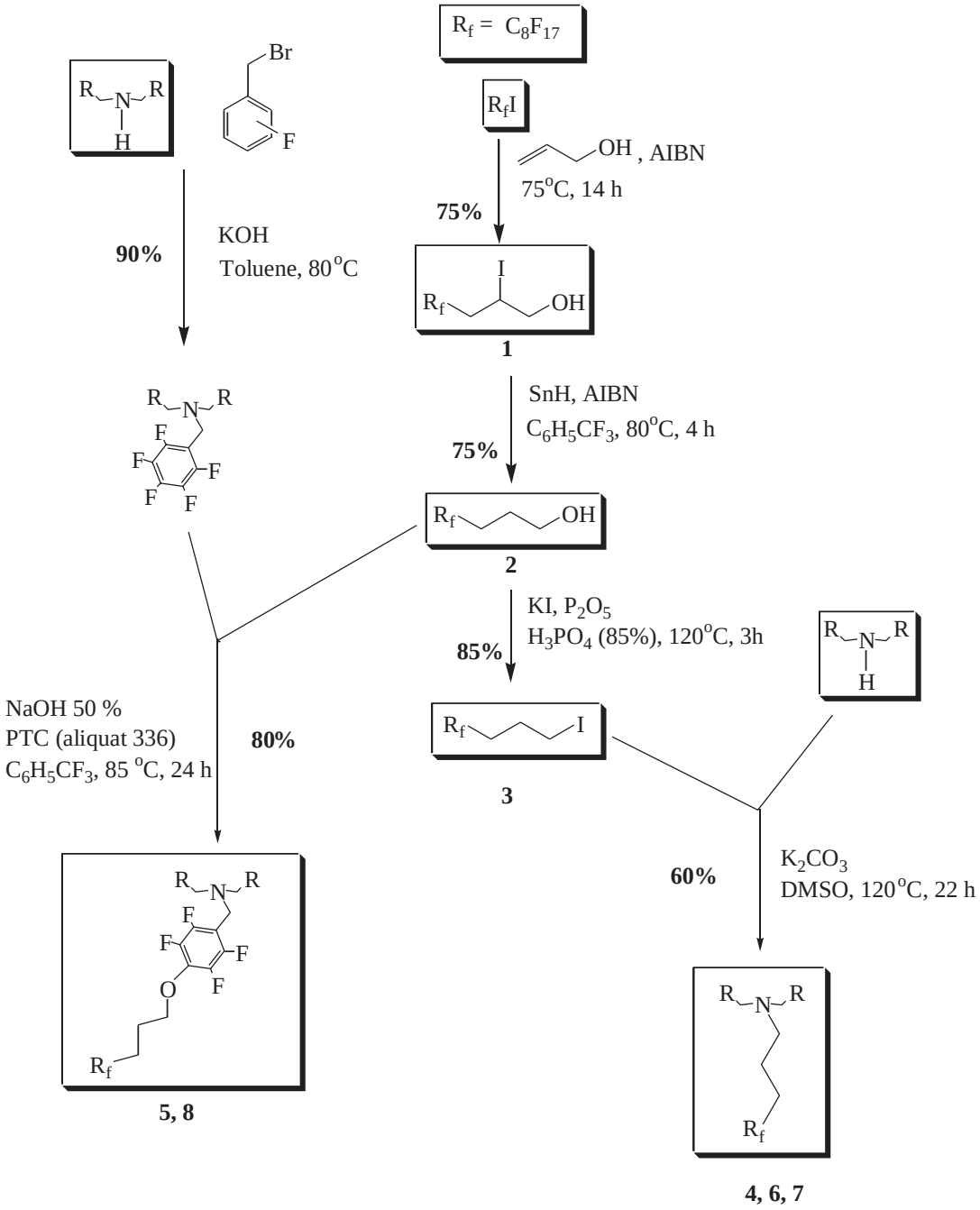
Functionalization of alkanes and alkenes utilizing in situ generated $[R_fMn(R_fTACN)]^{2+}$ and $[R_fCo(R_fTACN)]^{2+}$ (complexes 11 and 12) as precatalysts

The FBC oxidation results for several substrates are presented in Table 1. All the experiments were carried out under biphasic conditions, generating complexes **11** or **12**, in situ in perfluoroheptane (Scheme 2), while the upper phase was the substrate itself. Importantly, the oxidation products were detected only in the colorless upper phase after decantation (GC), while the colored perfluoroheptane lower phase contains only traces (<5%) of product. Clearly, a facile and rapid separation of the products from the catalyst was achieved using this FBC approach.

Table 1 demonstrates that the olefin with allylic hydrogens, cyclohexene, provides the highest % yield of oxidation products (650%/TBHP in 3 h) with TBHP–O_2, while alkane oxidation was much lower as noted with cyclohexane to cyclohexanol–cyclohexanone (CyOH–CyONE, 12%/TBHP in 24 h) and toluene to benzyl alcohol–benzaldehyde ($PhCH_2OH$–PhCHO, 65%/TBHP in 24 h). In the presence of **11**, TBHP, and O_2 (1 atm (1 atm = 101.325 kPa)), and under vigorous stirring, cyclohexene was converted to a product ratio of 2-cyclohexen-1-one (CyenONE, ~65%), 2-cyclohexen-1-ol (CyenOH, ~35%), and a small amount of cyclohexene oxide (<2%), while with complex **12** similar oxidation results were obtained.

It is also important to note that styrene, with no allylic hydrogens, was not converted to styrene epoxide under these biphasic conditions. *In the absence of O_2 or TBHP, only negligible amounts of CyenOH and CyenONE were detected,*

Scheme 1. Preparation of fluoroponytailed synthon **3** and alkylation to provide ligands **4**–**8**.



indicative of an autoxidation reaction, i.e., both were necessary for oxidation to proceed. At the end of the reaction, the upper phase was removed and new aliquots of cyclohexene and TBHP were added to provide a 400% yield after 5 h, showing that the catalyst, after decantation, was only present in the lower fluorocarbon phase.

Autoxidation mechanism and fate of the Mn^{2+} precatalyst

The presented results are in agreement with an autoxidation mechanism involving alkoxy (RO·) or alkylperoxy (ROO·) radicals (11), where the reaction was initiated by *t*-BuO· or *t*-BuO_2· radicals produced from redox reactions (Haber–Weiss process with Mn^{2+}/Mn^{3+}). In the case of the substrate cyclohexene, the allylic radical that formed was then trapped by O_2 ($k > 1 \times 10^9$ M^{-1} s^{-1}) to provide cyclohexenylperoxy radicals, which were able (ROO-H = 90 kcal mol^{-1}) to homolytically remove a hydrogen from benzylic or allylic C—H bonds (85 kcal mol^{-1}), and hence, propagate the radical reactions. The secondary cyclohexenyl hydroperoxide that was formed then decomposes catalytically in the presence of the $R_fMn(R_fTACN)$ catalyst to give the alcohol and the ketone products (12). Scheme 3 defines the initiation, propagation, termination, and product-forming steps for the sequence of reactions (eqs. [1]–[8]).

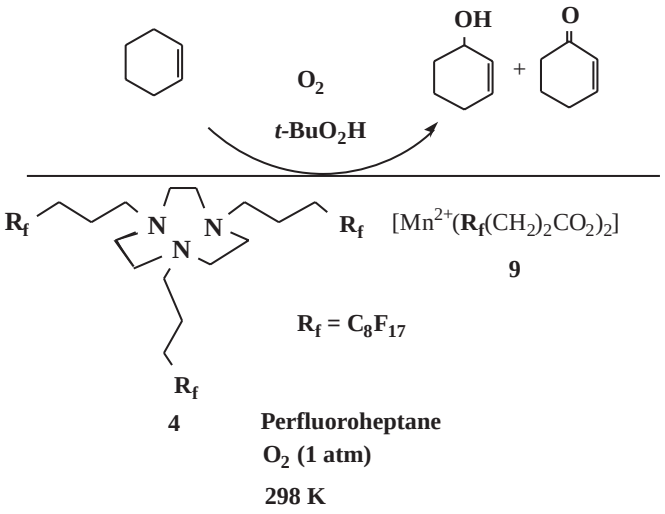
Moreover, the lower yields observed in the case of cyclohexane are consistent with the stronger C—H bond strength

Table 1. Alkene and alkane functionalization under fluorous biphasic catalysis conditions.[a]

Precatalyst	Substrate	Oxidant	Products (μmol)	Yield (%)[b]	*t* (h)
11	Cyclohexene	TBHP–O_2	CyenOH (160) CyenONE (300)	650	3
11	Cyclohexene	TBHP	CyenOH (<2) CyenONE (<2)		7
11	Cyclohexene	O_2	CyenOH (<1) CyenONE (<1)		24
9	Cyclohexene	TBHP–O_2	CyenOH (130) CyenONE (160)	360	12
11	Styrene	TBHP–O_2	no epoxide		24
11	Toluene	TBHP–O_2	PhCHO (15) PhCH2OH (30)	65	24
11	Cyclohexane	TBHP–O_2	CyOH (5) CyONE (3.5)	12	24
12	Cyclohexene	TBHP–O_2	CyenOH (185) CyenONE (360)	750	20
12	Cyclohexane	TBHP–O_2	CyOH (7) CyONE (5.5)	17	24

[a]Conditions: [$M(R_f(CH_2)_2CO_2)_2$] (3.5 μmol), Mn or Co, and the R_fTACN ligand (3.5 μmol) were dissolved in hot perfluoroheptane (3 mL) and then the substrate (2 mL) was added. The reaction starts after the addition of TBHP (90%, 72 μmol) under an O_2 atmosphere at ambient termperature.
[b]Total yield was based on TBHP added.

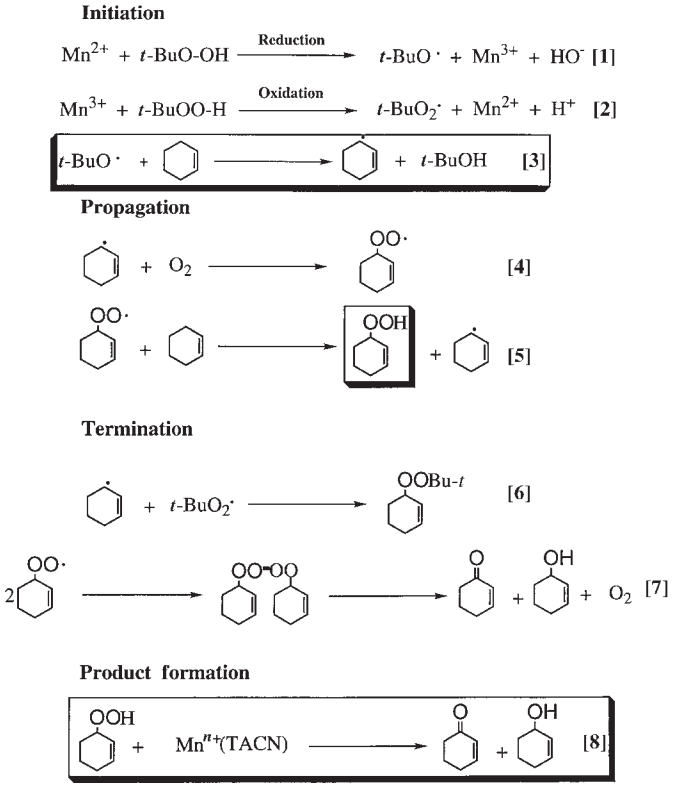
Scheme 2. Fluorous biphasic oxidation catalysis with cyclohexene as the substrate and complex **11** formed in situ from **4** and **9**.



(95 kcal mol^{-1}) (11), which implicates the cyclohexylperoxy radical, and thus causes a lowering of the rate of the propagation step. The chain termination step presumably comes mainly from the coupling of two cyclohexenylperoxy radicals to give alcohol, ketone, and O_2 (Russell-type mechanism (Scheme 3, eq. [7])) (11).

We found that the [R_fMn(R_fTACN)] complex, formed during the oxidation of **11**, was plausibly a $R_fMn^{3+}Mn^{4+}$ dimer. Therefore, when TBHP was added to the reaction mixture, the solution turns brown, and exhibits intense UV–vis absorptions (ε per atom is ~9000 and 1130 M^{-1} cm^{-1} at 300 and 500 nm, respectively, after 1 h) characteristic of dinuclear $Mn^{3+}Mn^{3+}$, $Mn^{3+}Mn^{4+}$, or $Mn^{4+}Mn^{4+}$ complexes (13). The occurrence of such a putative $R_fMn^{3+}Mn^{4+}$ dimer from starting complex **11** (Fig. 1, top spectrum), under oxidation conditions, was unambiguously confirmed by ESR studies at 9 K. Thus, a strong, distinctive 16-line signal of an antiferromagnetically coupled $R_fMn^{3+}Mn^{4+}$ dimer complex at $g = 2$ was observed in the perfluoroheptane phase, after 1 h of reaction in the presence of TBHP–O_2 and cyclohexene (Fig. 1, middle spectrum). Indeed, it has recently been shown that the decomposition of TBHP in the presence of a dinuclear

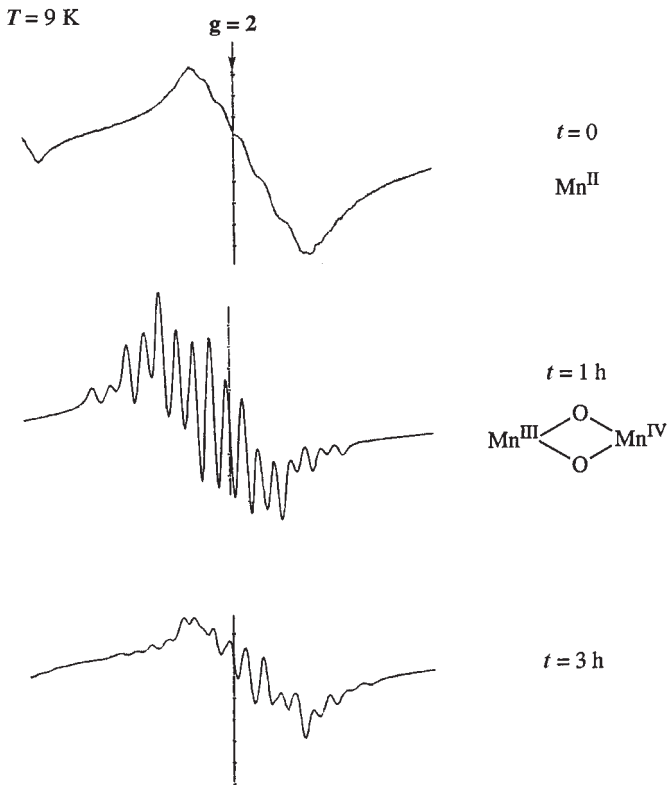
Scheme 3. Initiation, propagation, termination, and product forming steps with cyclohexene as substrate.



Mn_2^{3+}(2-OHsalpn)$_2$ complex resulted in the formation of *t*-BuO· radicals and a dinuclear $Mn^{3+}(\mu\text{-}O)_2Mn^{4+}$ complex (14).

Furthermore, rxn. [1] (Scheme 3) was favored over rxn. [2] with complex **11** for two important reasons: (*i*) it has been previously shown that in nonpolar solvents, eq. [2] was found to be very slow (15); and (*ii*) the $R_fMn^{3+}Mn^{4+}$ dimeric species formed upon the addtition of TBHP to complex **11** was not very efficient in the oxidation of TBHP. Interestingly, after 3 h (Fig. 1, lower spectrum), the 16-line ESR signal had almost disappeared, suggesting that this $R_fMn^{3+}Mn^{4+}$ dinuclear mixed valent species might be involved in the catalytic decomposition of the cyclohexenyl hydroperoxide intermediate to provide the alcohol and ketone products.

Fig. 1. ESR experiments at 20 K and 9 K (see *Experimental* for details). Top spectrum: $[R_fMn(R_fTACN)]^{2+}$ complex (**11**) at 20 K in benzotrifluoride; middle: after addition of TBHP–O_2 and cyclohexene (9 K); lower: after 3 h of reaction (9 K).



Conclusions

Finally, as we have clearly shown in this contribution, as well as being pointed out recently by Pozzi et al. (16), despite the apparent simplicity of the FBC concept, the concrete demonstration of this strategy is still a difficult challenge, since the solubilization of the fluoroponytailed metal complexes used in perfluorocarbons is one limiting step along with catalyst stability and the favorable recycling of the catalyst system. Thus, we were able to successfully solubilize complexes **11** and **12** in perfluoroheptane, using both the new R_fTACN ligand **4**, and the new R_fMn^{2+} and R_fCo^{2+} complexes **9** and **10**, with fluoroponytailed carboxylate ligands. Moreover, we have been able to perform alkane and alkene oxidations under FBC conditions in the presence of TBHP and O_2 as oxidants, and hence, separate the products from the catalyst by a simple decantation process. The oxidation process occurs via an autoxidation mechanism, with formation of alkenyl or alkyl hydroperoxides as the key intermediates, which then are catalytically decomposed by the R_fMn– or R_fCo–R_fTACN catalyst, probably at the solvent interface, to provide the alcohol and ketone products. Future studies will attempt to further the scope of the FBC approach to oxidation chemistry.

Experimental

Materials and instrumentation

The fluorocarbon solvents and some starting perfluoro derivatives were purchased from Pierce Chemical Co., while the alkenes and alkanes were from Aldrich Chemical Co. The oxidant, *tert*-butyl hydroperoxide (70% TBHP) was a commercial product from Aldrich Chemical Co., and all were used without further purification. The ^{1}H NMR spectra were obtained on a 500 MHz Brucker NMR spectrometer, while GC and GC–MS analysis were performed on Hewlett–Packard (HP) instruments. The UV–vis spectra were recorded on an HP diode array instrument with accompanying software. The ESR experiments were performed at the Calvin Laboratory at LBNL and the following describes the equipment used. EPR spectra were collected on a Varian E-109 spectrometer with an E-102 microwave bridge. The EPR spectra were collected using a home built signal averager and stored for further analysis on a VAX 4000-300. Samples were maintained at cryogenic temperatures using an Air Products Heli-tran liquid helium cryostat. For detecting the Mn^{2+} complex the conditions were as follows: 3300 ± 1000 G scan range, 10 mW microwave power, 20 K temperature, 32 G modulation amplitude, 100 kHz modulation frequency, 2 min/scan, 0.25 s time constant. Spectrometer conditions were as follows for detecting the 16 line spectrum from the coupled binuclear Mn^{3+}/Mn^{4+} complex: 2800 ± 500 G scan range, 30 mW microwave power, 9 K temperature, 32 G modulation amplitude, 100 kHz modulation frequency, 0.25 s time constant, 9.26 GHz microwave frequency. The amplitudes were calculated from the low-field and high-field peak-to-trough amplitudes for each designated peak.

2-Iodo-1-perfluorooctyl-3-propanol (1)

The R_fI ($R_f = C_8F_{17}$, 7 g, 12.8 mmol), allyl alcohol (1 mL, 14.7 mmol), and AIBN (84 mg, 0.51 mmol) were heated at 70–75°C under an inert atmosphere for 14 h. Every 2 h, a new portion of AIBN was added to the reaction mixture. The pale yellow solid obtained was recrystallized in refluxing hexane (40 mL). Compound **1** was obtained in 75% yield, mp 93–94°C. EI-MS: [M+] 604. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 4.45 (m, 1H, -C*H*I-), 3.79 (m, 2H, -C*H*$_2$-OH), 2.9 (2m, 2H, R_f-C*H*$_2$), 2.04 (t, -O*H*). Elemental anal. calcd. for $C_{11}H_6F_{17}IO$: C 21.87, H 1.00; found: C 22.06, H 0.97.

3-Perfluorooctyl-1-propanol (2)

Compound **1**, $R_fCH_2CHICH_2OH$ (8 g, 13.2 mmol), and AIBN (52 mg, 0.31 mmol) were partially dissolved in dry trifluorotoluene (40 mL). The tributyltin hydride (4.2 mL, 15.8 mmol) was then added dropwise and the reaction mixture was heated at 80°C under an inert atmosphere for 4 h (reaction followed by GC). After removing the solvent under vacuum, the resulting residue was dissolved in a perfluoroheptane–toluene mixture. After decantation, the lower phase was separated from the upper one, which mainly contains $(Bu)_3SnI$. By removing the perfluoroheptane, compound **2** was isolated as a white powder in 75% yield. Compound **2** can be recrystallized from hexane. EI-MS: [M+] 477. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 3.75 (m, 2H, -CH_2-OH), 2.20 (m, 2H, Rf-CH_2-), 1.88 (m, 2H, -CH_2-

CH_2-CH_2-), 1.57 (s, -OH). Elemental anal. calcd. for $C_{11}H_7F_{17}O$: C 27.63, H 1.46; found: C 27.72, H 1.63.

3-Perfluorooctyl-1-iodopropane (3)

The phosphorous pentaoxide (3.4 g) was added to phosphoric acid (85%, 7.1 mL) in a 50 mL round-bottom flask and then the mixture was cooled to 0°C. The KI (1.39 g, 8.2 mmol) was first added, followed immediately by $R_fCH_2CH_2CH_2OH$ (1.5 g, 3.1 mmol). The mixture was heated at 120°C for 3.5 h. At ambient temperature, 10 mL of water was added, and the resulting brown solution was extracted four times with 25 mL of diethyl ether. The organic layer was washed twice with 25 mL thiosulfate (0.1 M), then dried over Na_2SO_4. After removing the solvent, the iodo derivative was obtained as an oil, which solidified at 4°C. Compound **3** was used without further purification (yield 85%); however, **3** can be recrystallized from methanol. EI-MS: [M+] 588. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 3.26 (t, 2H, I-C*H*$_2$-), 2.16 (2m, 4H, -C*H*$_2$-C*H*$_2$-R_f). Elemental anal. calcd. for $C_{11}F_{17}H_6I$: C 22.47, H 1.02; found: C. 22.80, H 1.26.

Tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (4)

The TACN (88.4 mg, 0.73 mmol), K_2CO_3 (423 mg, 3.1 mmol), and $R_fCH_2CH_2CH_2I$ (1.41 g, 2.41 mmol) were dissolved in DMSO (10 mL, distilled over CaH_2) and heated at 90°C for 24 h. Then perfluoroheptane (20 mL) was added to the reaction mixture and the brown fluorous lower phase was separated and then filtered. After removing the solvent, compound **4** was obtained as a brown oil. After crystallization from hot hexane, compound **4** was isolated as a yellowish powder in 50% yield. FAB-MS: [M + H$^+$] 1510. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 2.71 (s, 12H, -N-C*H*$_2$-C*H*$_2$-N), 2.55 (t, 6H, -N-C*H*$_2$-C*H*$_2$-), 2.17 (m, 6H, -CH_2-C*H*$_2$-CH_2), 1.58 (m, 6H, -CH_2-C*H*$_2$-Rf). Elemental anal. calcd. for $C_{39}H_{30}F_{51}N_3$: C 31.03, F 64.20, H 1.98, N 2.78; found: C 30.74, F 64.31, H 2.02, N 2.70.

Synthesis of the *N*-(pentafluorotoluene)-bis-picolylamine and ligand 5

This procedure for the preparation of **5** was similar to that used to prepare ligand **8**. At the end of the reaction, the toluene was removed under vacuum, and a brownish solid was obtained. This solid was triturated with pentane affording a beige powder. Ligand **5** was obtained in 85% yield and provided a satisfactory ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 8.52 (d, 2H, aromatic H), 7.65 (t, 2H, aromatic H), 7.51 (d, 2H, aromatic H), 7.15 (m, 2H, aromatic H), 3.90 (s, 2H, -CH_2-C_6F_5), 3.85 (s, 4H, -C*H*$_2$-C_5H_4N).

Synthesis of ligand 6

BPA (59 mg, 0.296 mmol), K_2CO_3 (57 mg,), $R_fCH_2CH_2CH_2I$ (191 mg, 0.325 mmol) in DMSO (0.5 mL, distilled over CaH_2) were heated at 90°C for 16 h. The reaction mixture was filtered and the solvent removed in vacuo. Ligand **6** was purified by alumina column chromatography (CH_2Cl_2–MeOH) and was recovered as a beige oil, which solidifies at 4°C providing a yield of 60%. Ligand **6** was found to be soluble in hot, but not in cold perfluoroheptane. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 8.54 (d, 2H, pyr), 7.66 (t, 2H, pyr), 7.46 (d, 2H, pyr), 7.16 (m, 2H, pyr), 3.83 (s, 4H, -N-CH_2-pyr), 2.63 (t, 2H, -N-C*H*$_2$-CH_2-), 2.03 (m, 2H, -CH_2-C*H*$_2$-CH_2), 1.76 (m, 2H, -CH_2-C*H*$_2$-Rf). FAB-MS : [M + H$^+$] 660.

Synthesis of ligand 7

The BisPicen (50 mg, 0.206 mmol), K_2CO_3 (80 mg, 0.580 mmol), and $R_fCH_2CH_2CH_2I$ (266 mg, 0.450 mmol) were dissolved in DMSO (2.5 mL, distilled over CaH_2) and then heated at 90°C for 24 h. The solvent, benzotrifluoride, was added at room temperature to dissolve a brown oil, and then the solvent was removed under vaccum. To the sticky residue was added dichloromethane and then the solution was filtered, and the solvent removed under vaccum. The ligand (**7**) was purified first by alumina column chromatography (CH_2Cl_2–MeOH) and then by recrystallization from hexane to obtain a yellowish powder in 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 8.54 (d, 2H, pyr), 7.66 (t, 2H, pyr), 7.46 (d, 2H, pyr), 7.16 (m, 2H, pyr), 3.83 (s, 4H, -N-CH_2-pyr), 2.63 (t, 2H, -N-C*H*$_2$-CH_2-), 2.03 (m, 2H, -CH_2-C*H*$_2$-CH_2), 1.76 (m, 2H, -CH_2-C*H*$_2$-R_f). FAB-MS: [M + H$^+$] 1163. Anal. calcd. for C_{36} H_{28} N_4 F_{34}: C 37.2, H 2.40, N 4.82; found: C 36.51, H 2.33, N 4.38.

Synthesis of tris-*N*-pentafluorophenyl-1,4,7-triazacyclononane and ligand 8

To a stirring solution of TACN (3.7 mmol) in anhydrous toluene (10 mL) in a glovebox was added powdered KOH (11 mmol) slowly, and then the resulting suspension was treated with $C_6F_5CH_2Br$ (11 mmol) dropwise. The reaction mixture was heated to 80°C and stirred at this temperature for 8 h. After being cooled to room temperature, it was then treated with an additional portion of powdered KOH and then $C_6F_5CH_2Br$. The mixture was stirred and heated to 80°C for another 8 h. After filtration, the toluene is removed under vacuum leading to a yellow solid, which gave a satisfactory NMR spectrum. Tris-*N*-pentafluorophenyl-1,4,7-triazacyclononane can be further purified by recrystallization from MeOH; mp 75°C. EI-MS: [M+] 669. ^{1}H NMR (400 MHz, $CDCl_3$, 25%C) δ: 2.70 (s, 12H, -CH_2-TACN), 3.71 (s, 6H, -CH_2-Ph). ^{13}C NMR (MHz, $CDCl_3$, 25°C) δ: 48.31, 54.69, 135.99, 138.50, 144.63, 146.62. ^{19}F NMR (MHz, $CDCl_3$–$CFCl_3$, 25°C) δ: –142.82 (2F), –156.11 (1F), –162.91 (2F). Elemental anal. calcd. for $C_{28}H_{18}F_{15}N_3$: C 48.4, F 42.5, H 2.7, N 6.3; found: C 48.3, F 42.4, H 2.8, N 6.2.

The PTC catalyst, Aliquat 336 (49 μmol), trifluorotoluene (5 mL), tris-*N*-pentafluorophenyl-1,4,7-triazacyclononane (1.49 mmol), $R_fCH_2CH_2CH_2OH$ (4.92 mmol), and NaOH 50% (5 mL) were stirred at 85°C for 22 h. After removing the solvent in vacuo, the solid was taken off with a mixture of trifluorotoluene, dichloromethane, and water. After stirring, the cloudy organic phase was isolated and the solvent stripped in vacuo. After washing the resulting orange solid with dichloromethane, compound **8** was obtained, after filtration, as a white powder (80%). Compound **8** can be further purified by alumina gel chromatography (CH_2Cl_2–MeOH, 0–2%). m p 98°C. FAB-MS: [M+H$^+$] 2044. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ: 4.27 (t, 6H, -O-CH_2-), 3.68 (s, 6H, N-CH_2-C_6F_4), 2.71 (s, 12H, CH_2-TACN), 3.37 (m, 6H, O-CH_2-C*H*$_2$), 2.10 (m, 6H, -CH_2-C*H*$_2$-Rf). ^{13}C NMR (MHz,

$CDCl_3$, 25°C) δ: 48.31, 54.69, 135.99, 138.50, 144.63, 146.62. ^{19}F NMR (MHz, $CDCl_3$–$CFCl_3$, 25°C) δ: –81.29 (3F), –114.92 (2F), –122.23 (2F), –122.43 (4F), –123.23 (2F), –124.00 (2F), –126.63 (2F), –144.16 (2F), –158.19 (2F). Anal. calcd. for $C_{60}H_{36}N_3F_{63}O_3$: C 35.3, H 1.8, N 2.1, F 58.6; found: C 35.6, H 1.9, N 2.1, F 59.6.

$[Mn(C_8F_{17}(CH_2)_2CO_2)_2(H_2O)_2]$ (9)

The $CF_3(CF_2)_7CH_2CH_2CO_2H$ (1.35 g, 2.80 mmol) was dissolved in acetone (15 mL) and to this solution was added triethylamine (380 mL, 2.80 mmol). This resulting solution was added dropwise to $Mn(ClO_4)_2 \cdot 6H_2O$ (500 mg, 1.37 mmol) dissolved in acetone (30 mL). The sticky precipitate which formed was vigorously stirred for 2 h. After filtration, **9** was obtained as a white powder in 75% yield. Elemental anal. calcd. for $C_{22}F_{34}H_{12}O_6Mn$: C 24.61, F 60.19, H 1.12, Mn 5.12; found: C 25.37, F 59.77, H 0.94, Mn 5.50.

$[Co(C_8F_{17}(CH_2)_2CO_2)_2(H_2O)_2]$ (10)

The same procedure, as conducted with complex **9**, was used for the synthesis of **10**, except with $Co(ClO_4)_2 \cdot 6H_2O$. A pink precipitate formed immediately, and after filtration, a pink powder was obtained in 100% yield. Elemental anal. calcd. for $C_{22}H_{12}F_{34}CoO_6$: C 24.53, H 1.11, F 59.98, Co 5.46; found: C 25.05, H 1.27, F 60.15, Co 5.35.

ESR–FBC experiment

The ESR spectrum for in situ generated **11** was conducted at 20 K in benzotrifluoride (top spectrum, Fig. 1). Using standard oxidation conditions for cyclohexene as outlined in Table 1, aliquots of the perfluoroheptane layer were removed and immediately frozen at 100 K in an ESR tube (middle and lower spectra, Fig. 1). ESR spectra were recorded at 9 K using microwave power at 10 mW, modulation amplitude 32 G, a time constant of 0.5 s, at a frequency of 9.18 GHz, and gain of 3.2×10^{-3}.

Acknowledgment

The studies at LBNL were generously supported by a gift grant (R.H.F.) and a postdoctoral fellowship to J.-M. V. from Elf Aquitaine Inc., and the Department of Energy under Contract no. DE-AC03–76SF00098. We thank Dr. István T. Horváth and Dr. Jozsef Rábai for many helpful discussions concerning our FBC program.

References

1. I. T. Horváth and J. Rábai. Science (Washington, D.C.), **266**, 72 (1994), and refs. therein.
2. M. Vogt. Ph.D Thesis. Technical University of Aachen, 1991.
3. (*a*) I.T. Horváth. Acc. Chem. Res. **31**, 641 (1998) and refs. therein; (*b*) I.T. Horváth. *In* Applied homogeneous catalysis with organometallic compounds. *Edited by* B. Cornils, W.A. Hermann). VCH, 1996. p. 601; (*c*) E. de Wolf, G. van Koten, and B.-J. Deelman. Chem. Soc. Rev. **28**, 37 (1999); (*d*) R.H. Fish. Chem. Eur. J. **5**, 1677 (1999), and refs. therein.
4. M. Hudlicky and A.E. Pavlath. Chemistry of organic compounds II. Ellis Horwood, Chichester, U.K. 1992.
5. K. Neimann, R. Neumann, A. Rabion, R.M. Buchanan, and R.H. Fish. Inorg. Chem. **38**, 3575 (1999), and refs. therein.
6. J.-M. Vincent, A. Rabion, V.K. Yachandra, and R.H. Fish. Angew. Chem. Int. Ed. Engl. **36**, 2346 (1997).
7. G. Pozzi, M. Cavazzini, S. Quici, and S. Fontana. Tetrahedron Lett. **38**, 7605 (1997).
8. (*a*) S. Ménage, M.-N. Collomb-Dunand-Sauthier, C. Lambeaux, and M. Fontecave. J. Chem. Soc. Chem. Commun. 1885 (1994); (*b*). D. De Vos and T. Bein. J. Chem. Soc. Chem. Commun. 917 (1996).
9. M. Kotora, M. Hajek, B. Ameduri, and B. Boutevin. J. Fluorine Chem. **68**, 85 (1994).
10. P. Mathur and G. Dismukes. J. Am. Chem. Soc. **105**, 7093 (1983).
11. R.A. Sheldon and J. K. Kochi. Metal-catalyzed oxidations of organic compounds. Academic Press, New York. 1981.
12. R.H. Fish, M.S. Konings, K.J. Oberhausen, R.H. Fong, W.M. Yu, G. Christou, J.B. Vincent, D.K. Coggin, and R.M. Buchanan. Inorg. Chem. **30**, 3002 (1991).
13. Y.-M. Frappart, A. Boussac, R. Albach, E. Anxolabéhère-Malhart, M. Delroisse, J.-B. Verlhac, G. Blondin, J.-J. Girerd, J. Guilhem, M. Cesario, A.W. Rutherford, and D. Lexa. J. Am. Chem. Soc. **118**, 2669 (1996).
14. M.T. Caudle, P. Riggs-Gelasco, A.K. Gelasco, J.E. Penner-Hahn, and V.L. Pecoraro. Inorg. Chem. **35**, 3577 (1996).
15. R.A. Sheldon and J.K. Kochi. Adv. Catal. **25**, 272 (1976).
16. G. Pozzi, S. Banfi, A. Manfredi, F. Montanari, and S. Quici. Tetrahedron, **52**, 36, 11 879 (1996).